

REPORT DOCUMENTATION PAGE

AD-A209 290

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE		1b. RESTRICTIVE MARKINGS	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited.	
6a. NAME OF PERFORMING ORGANIZATION Xerox Webster Research Center		5. MONITORING ORGANIZATION REPORT NUMBER(S) ARO 22292.8-EL	
6b. OFFICE SYMBOL (If applicable) -		7a. NAME OF MONITORING ORGANIZATION U. S. Army Research Office	
6c. ADDRESS (City, State, and ZIP Code) 800 Phillips Road, 0114-41D Webster, NY 14580		7b. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION U. S. Army Research Office		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAL03-86-C-0003	
8b. OFFICE SYMBOL (If applicable)		10. SOURCE OF FUNDING NUMBERS	
8c. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Pulsed Laser Processing of CdTe and Other II-VI Compound Semiconductor/Metal Interfaces			
12. PERSONAL AUTHOR(S) L.J. Brillson			
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM 11-01/85 TO 4/30/89	
		14. DATE OF REPORT (Year, Month, Day) 01/15/89	
		15. PAGE COUNT 18	
16. SUPPLEMENTARY NOTATION The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		CdTe, CdSe, CdS, Metal-Semiconductor Interfaces, laser annealing, chemical reaction, diffusion, deep levels, defects, Schottky barriers, luminescence, soft x-ray photoemission, aging, MBE	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) See reverse side.			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/DUNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	
		22c. OFFICE SYMBOL	

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

We demonstrate that the chemical and electronic properties of the metal/CdTe or other II-VI compound semiconductor are closely related and that atomic-scale processing techniques can be useful in controlling both the metallurgical and the Schottky barrier features of the interface. Pulsed laser processing combined with surface science techniques revealed microscopic chemical interactions at elevated temperatures for representative metal-semiconductor junctions. Optical spectroscopy techniques showed that such chemical interactions produced changes in the deep electronic levels within the semiconductor band gap. Carefully controlled measurements of both chemistry and electronics under UHV conditions established that the E_f stabilization within the semiconductor band gap was dominated by the presence of these deep levels. Essentially, these deep levels are the link between interface chemistry and Schottky barrier formation. By suppressing this chemical interaction, we were able to control the semiconductor band bending over a much wider range than hitherto possible, achieving the lowest p-type barriers to nondegenerately-doped CdTe reported to date. Finally, we have shown that these studies can be extended to CdTe films grown by MBE. For these higher quality crystals, we should be able to optimize growth and device properties with even less interference from deep levels. These results offer multiple new opportunities for further improving the chemical and electrical stability, as well as the absolute Schottky barrier heights of metal contacts to CdTe and other II-VI compound semiconductors.



Accession For	
NTIS GEA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

**PULSED LASER PROCESSING OF CdTe AND OTHER II-VI COMPOUND
SEMICONDUCTOR / METAL INTERFACES**

FINAL REPORT

L.J.BRILLSON

APRIL 30, 1989

U.S.ARMY RESEARCH CENTER

CONTRACT # DAAL03-86-C-0003

XEROX WEBSTER RESEARCH CENTER

**APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED**

THE VIEW, OPINIONS, AND / OR FINDINGS CONTAINED IN THIS REPORT ARE THOSE OF THE AUTHOR AND SHOULD NOT BE CONSTRUED AS AN OFFICAL DEPARTMENT OF THE ARMY POSITION, POLICY, OR DECISION, UNLESS SO DESIGNATED BY OTHER DOCUMENTATION.

Table of Contents

	Page
Cover Page	1
Table of Contents	2
Title and Abstract	3
Appendix List	4
Statement of the Problem Studied	5
Summary of the Most Important Results	6
Technical Papers Published Under Contract DAAL03-86-C-003	18
Participating Scientific Personnel and Advanced Degrees Earned	19
Appendices	20

Pulsed Laser Processing of CdTe and Other II-VI Compound Semiconductor /Metal Interfaces

Abstract

We demonstrate that the chemical and electronic properties of the metal / CdTe or other II-VI compound semiconductor are closely related and that atomic-scale processing techniques can be useful in controlling both the metallurgical and the Schottky barrier features of the interface. Pulsed laser processing combined with surface science techniques revealed microscopic chemical interactions at elevated temperatures for representative metal-semiconductor junctions. Optical spectroscopy techniques showed that such chemical interactions produced changes in the deep electronic levels within the semiconductor band gap. Carefully controlled measurements of both chemistry and electronics under UHV conditions established that the E_D stabilization within the semiconductor band gap was dominated by the presence of these deep levels. Essentially, these deep levels are the link between interface chemistry and Schottky barrier formation. By suppressing this chemical interaction, we were able to control the semiconductor band bending over a much wider range than hitherto possible, achieving the lowest p-type barriers to nondegenerately-doped CdTe reported to date. We have now extended these studies to higher quality CdTe films grown by molecular beam epitaxy. These results offer several new opportunities for further improving the chemical and electrical stability, as well as the absolute Schottky barrier heights of metal contacts to CdTe and other II-VI compound semiconductors.

Appendices: Technical Publications

1. **Modification of Electronic and Chemical Structure at Au and In - CdTe Interfaces by Pulsed Laser Annealing**, by J.L. Shaw *et al.*
2. **Interfacial Deep Level Formation and Its Effect on Band Bending at Metal/CdTe Interfaces**, by J.L.Shaw *et al.*
3. **Cathodoluminescence Spectroscopy of Metal-Semiconductor Interface Structures**, by L.J.Brillson *et al.*
4. **Deep Level Formation and Band Bending at Metal/CdTe Interfaces**, by J.L.Shaw *et al.*
5. **Unpinned Schottky Barrier Formation at Metal/GaAs Interfaces**, by L.J.Brillson *et al.*
6. **Chemically Controlled Deep Level Formation and Band Bending at Metal-CdTe Interfaces**, by J.L.Shaw *et al.*
7. **Influence of Deep States on GaAs and CdTe-Metal Interface Formation**, by J.L.Shaw *et al.*
8. **Deep Levels and Band Bending at Metal-Semiconductor Interfaces**, by L.J.Brillson *et al.*
9. **Interdiffusion, Interfacial State Formation, and Band Bending at Metal/CdTe Interfaces**, by J.L.Shaw *et al.*

Statement of the Problem Studied

CdTe and other II-VI compound semiconductors are of considerable interest for device applications because of their photoelectronic properties. CdTe is also used in device structures with the ternary alloy HgCdTe, which has a variable band gap that can be adjusted from the visible into the infrared region. Such material has been demonstrated to yield extremely sensitive infrared detectors and image arrays. Electrical contacts to these materials are of importance not only in terms of supplying power to or carrying signals away from the semiconductor, but also as an integral part of active elements for preprocessing information from the optical sensor on the sensing cell itself.

We used pulsed laser annealing to study diffusion, chemical reaction, and associated electronic processes at metal interfaces with CdTe and other II-VI compound semiconductors. Because of the extremely short time scale of the laser pulse and the attendant heating, movement of metal and semiconductor atoms could be limited to tens of Å. In this way, changes in interface chemical structure at elevated temperature could be monitored by surface science techniques in discrete steps and without a "washing out" of the interface structure below the detectability of our spectroscopic tools. These studies were carried out by metal deposition on to clean semiconductor surfaces in an ultrahigh vacuum (UHV) environment such that ambient contamination which could interfere with or otherwise mask the metal - semiconductor reactions was excluded. At each stage of the contact interaction, a variety of surface science techniques was used to follow atomic movements on a monolayer scale and to determine the chemical state of the atoms. Spectroscopic techniques were also used to identify changes in interface

electronic structure induced by the laser annealing. These chemical and electronic structure changes were then related to electrical characteristics obtained from *in-situ* diode measurements. The effects of intermediate layers on the laser-induced processing was investigated for chemical trapping, doping, or formation of new dielectric layers only a few nanometers thick. From these studies of extremely short diffusion processing, we gained insight into the chemical kinetics and physics of diffusion processing, how these chemical changes could affect the Schottky barrier properties, how such diffusion could be optimized or controlled, and thus how contact degradation at elevated temperatures could be reduced.

Summary of the Most Important Results

We monitored the chemical and electronic properties of metal / CdTe and other II-VI compound during pulsed laser annealing by soft x-ray photoemission spectroscopy (SXPS). We promoted localized chemical reactions at Al interfaces with CdTe, CdSe, and CdS and examined the diffusion and bonding on an atomic scale as a function of laser energy density. We used a 30 nanosecond, 308 nm XeCl excimer laser to pulse-laser-anneal 20 Å Al overlayers on UHV-cleaved CdTe (110), CdSe (1010), and CdS (1010) surfaces. SXPS measurements reveal a well-defined threshold for the Al - CdTe reaction, with a bonding change of Al atoms from metallic to covalent, production of dissociated Cd, and metal-cation alloying. The entire Al film reacts over an energy density range of 0.17 to 0.3 J / cm² for CdTe, CdSe, and CdS respectively. In each case, a finite range of energy densities exist such that chemical reactions are promoted without major disruption of the film/ substrate morphology.

We examined the changes in electronic and chemical structure at laser - annealed Au - CdTe and In - CdTe interfaces using a complement of surface science techniques. We examined as-cleaved (110) CdTe surfaces in UHV and as a function of Au and In coverages. After deposition of 20 Å (metallic) layers, the structures were examined as they were annealed at various power densities with the pulsed excimer laser. Surface chemistry was monitored with XPS. Band bending was studied with SXPS and low energy cathodoluminescence (CLS). Reduced near-band-edge (NBE) cathodoluminescence emission relative to luminescence from deep levels provided an additional indication of increased band bending. CLS, photoluminescence (PL), and surface photovoltage (SPS) were used to detect bulk and surface defects.

Au / n-CdTe interfaces exhibited large Schottky barriers which were reduced by metal - semiconductor interdiffusion. SXPS and SPS measurements showed band bending induced by Au deposition which increased with coverage to 0.8 eV after 20Å. After aging, the interface at room temperature for 36 hours, SXPS core level shifts reveal a 0.4 eV reduction in band bending and significant Au-Cd intermixing. A similar interface aged for four days exhibited complete restoration of the NBE CL peak, indicative of reduced band bending. Laser annealing of the aged interface further reduced the band bending measured by SXPS and CLS.

In / p-CdTe interfaces exhibited dramatic changes in band bending with chemical phase formation induced by laser annealing. From a band bending in excess of 0.3 eV for the metallized surface, laser pulse powers of 0.1, 0.4, and 0.5 J/cm² increased the band bending by 0.1, 0.3, and 0.7 eV. Accompanying these increases were changes in In and Cd bonding, clearly showing bonded In (InTe) and metallic Cd. No chemical shifts of the Te features were observed.

The commercially available CdTe crystals we were using exhibited high densities of deep trap levels. Bulk and surface defects were determined with CL, PL, and SPS. Luminescence from a bulk defect was found in all samples studied, both n- and p-type, at 0.8 eV with room temperature CLS, PL, and SPS, and at 8 K below E_c . In addition, the CL spectra showed a broad band from a surface defect centered at 1.1 eV. This defect could be induced by deposition of both Au and In and by electron beam damage. SPS spectra showed that a similar defect was induced by Au deposition. These results indicated that CdTe single crystals provided by most commercial vendors have serious electronic deficiencies and emphasized the need for higher quality CdTe single crystals in electronic studies.

SXPS measurements of Cd 4d and Te 3d core levels with monolayer increments of metal on the UHV-cleaved CdTe (110) surface determined the atomic composition, chemical phases, and Fermi level movements of the evolving metal-semiconductor interface. CLS revealed optical emission from mid-gap levels produced by metallization and pulsed laser annealing as well as defect levels associated with the bulk semiconductor. The short (5 nsec) pulsewidth and high absorption of the 308 nm excimer laser permitted staged heating of the near surface region to temperatures as high as the melting point without significant interdiffusion. Correlation of these techniques demonstrated that metallization and thermal processing produced substantial electronic changes which were associated with chemical reaction and diffusion at the microscopic metal-semiconductor interface.

Au / CdTe interfaces exhibited metal-semiconductor interdiffusion and competing mechanisms of Schottky barrier formation. Au deposition on n-CdTe produced a gradual increase in band bending of 0.8 eV over 20 Å. Room temperature aging for

36 hours reduced the band bending by 0.4 eV. Changes in the width of the depletion layer reflected these changes in band bending as evidenced by a dramatic decrease of the CLS near-band-edge emission with Au deposition and a corresponding reappearance after aging. Laser annealing at 0.2 J / cm^2 returned the Fermi level E_f to its as-cleaved position. Changes in SXPS core level intensities showed a Te-rich surface segregation after metallization, aging, and annealing. In addition to a 0.8 eV mid-gap emission related to bulk defects, CLS spectra revealed an interface feature induced by Au and annealing at 1 eV which extended toward the conduction band edge. Consequently, the Te deficiency at the buried Au-CdTe interface appeared to produce donor-like states which reversed the Au-induced band bending.

In / CdTe interfaces exhibited band bending changes which depended directly on a thermally -activated chemical reaction. Submonolayer coverages of In on p-type CdTe caused a 0.3 eV E_f movement toward the conduction band with only a partial In-Te reaction. Additional In deposition produced no further E_f shift or reaction. Laser annealing induced additional chemical reaction (e.g., more strongly bound In interface atoms and evidence for Cd dissociation) and moved E_f an additional 0.7 eV toward the conduction band. Changes in both chemical bonding and band bending took place in two discrete stages with increasing laser energy density. CLS again indicated formation of interface states in the upper third of the band gap. Thus the In-Te chemical reaction could be linked directly with E_f movement and new gap states.

The striking contrast in E_f movements with metallization and processing of Au- and In-CdTe interfaces highlighted the sensitivity of contact properties to reaction and diffusion on an atomic scale. Thus pulsed laser annealing provides an effective tool

for promoting and modifying such chemical structure in ultrathin layers and thereby optimizing electronic structure at the intimate metal-semiconductor contact.

Optical emission and absorption spectroscopy analysis of CdTe surfaces under UHV conditions revealed that surface processing - wet chemical etching, gas exposure, ageing, and pulsed laser annealing- has major effects on the discrete levels located within the CdTe band gap and localized near the surface. These in turn have a dominant effect on the ultimate E_f position of CdTe Schottky barriers subsequently formed.

We performed low temperature PL measurements on CdTe single crystals from a wide array of vendors, including the Oregon Graduate Center, GalTech Inc., II-VI Inc., and Cleveland Crystals. UHV-cleaved rather than etched or air-exposed surfaces provided the basis for this comparison since we found that the latter were often dependent on the surface. Contaminated and poorly cleaved surfaces yielded PL spectra which were much less intense and which contained emission features different from PL spectra of UHV-cleaved CdTe surfaces of the same specimen. Luminescence from deep levels at 15 K of UHV-cleaved CdTe specimens was evident for CdTe from each and every vendor. At 15 K, CdTe peak features occurred at 1.4 eV and near the band edge (1.55-1.58 eV) for all specimens. In addition, peak features occurred at 0.65, 0.8, 1.0, 1.1, and 1.2 eV, depending upon the vendor. The luminescence intensity of these peak features varied by orders of magnitude from specimen to specimen. The 1.4 eV and near-band-edge luminescence intensities showed little or no correlation with the intensities of the deeper state emission intensities. Therefore, we may conclude that photoluminescence spectra restricted to only these higher energies do not provide a reliable indicator of the native defects,

impurities, or other crystal imperfections giving rise to the mid-gap emission features.

We used SPS to complement the PL measurements and to determine the position of the deep levels with respect to the band edges. SPS results revealed evidence for states located at 0.7, 1.0, and 1.4 eV (± 0.1 eV) above the valence band edge. These energies correlated with PL results and indicated that these PL transitions involve imperfections in the upper half of the band gap. The 1.4 eV PL feature was associated with a transition between a donor near the conduction band edge and an acceptor state 0.14 eV above the valence band edge.

The PL transition energies correlated with the Fermi level position observed by SXPS after metallization and laser processing. The final E_f position at the Au / CdTe interface corresponded to a very high PL intensity near 1.4 eV which increased further after laser processing. Three stages of E_f stabilization were found at the In / CdTe interface which also correlated with deep level transition energies found in that CdTe specimen. These results suggested that E_f was being "pinned" by defects created by chemical interaction at the metal interface. Although little is known about the origin of the 0.8 eV and 1.1 eV PL transitions, the 1.4 eV band has been related to Te deficiency (C.B.Norris and K.R.Zanio, J. Appl. Phys. 53, 6347 (1982)). The Cd/Te core level intensity ratios measured by SXPS for the chemical interaction between both In and Au and CdTe also indicated strong Te surface segregation. Thus a major consideration in forming electrical barriers with Fermi level stabilization in the lower part of the CdTe band gap must include controlling the Te concentration in the interface region.

We used reactive metal interlayers to suppress anion outdiffusion at Au-CdTe junctions and thereby to alter the formation of deep interfacial states. We found a dramatically reduced p-type band bending and, using SXPS and *in-situ* PL spectroscopies, we demonstrated that deep levels observed directly at the interface were responsible for the chemically-induced electrical behavior.

For metal interfaces with CdTe, interdiffusion is pronounced even at room temperature and is dominated by preferential Te outdiffusion. While the stoichiometry of compound semiconductor outdiffusion is known to influence interface electrical properties, it has not been possible to suppress this anion-rich intermixing for CdTe. Furthermore, while E_f positions in the semiconductor band gap have been shown to correlate with deep levels of CdTe defects, it has not been possible to control the creation of such states and thereby control the interface band bending. We used the recent discovery that reactive Yb interlayers are effective diffusion barriers at Al/Hg_xCd_{1-x}Te interfaces (D.J.Peterman *et al.*, J. Vac. Sci. Technol. A6, 1575 (1988)) to suppress preferential Te outdiffusion at CdTe interfaces for the first time. With this chemical control, we were able to control the formation of deep levels at these interfaces and thereby control electrical barrier formation.

SXPS and PL experiments were performed at 80 K on UHV-cleaved CdTe surfaces which were masked to permit Yb deposition on only one half of the clean (110) face, followed by Au deposition over the entire surface. This geometry permitted a direct comparison of electronic properties of chemically-inequivalent interfaces both on the same surface. SXPS results for the Au / 2 Yb monolayer/CdTe interface included a pronounced Yb-Te chemical reaction plus the formation of an atomically abrupt junction. In contrast, the Au/CdTe interface exhibited no pronounced reactions but

significant Te outdiffusion, even at low temperature. Cd outdiffusion at low temperatures was low for both junctions. Warming to room temperature enhanced the Te and Cd outdiffusion significantly for the Au/CdTe interface only.

The contrast in electronic properties was equally pronounced. SXPS rigid core level shifts show an E_f stabilization energy 1.1 eV above the valence band E_v for the interdiffused Au/CdTe interface *versus* 0.55 eV above E_v for the abrupt Au / Yb / CdTe junction. Thus the presence of an atomically -thin interlayer was responsible for decreasing the p-type band bending by over one-half volt. PL measurements of the intensity of exciton recombination confirmed this difference in band bending since, for PL excitation within the surface space charge region, the exciton recombination probability decreases strongly with increased band bending. With the Yb diffusion barrier, the Fermi level reached a value as low lower in the band gap than has ever been reported for a nondegenerately doped CdTe contact.

The interdiffused Au / CdTe interface produced new deep levels whose energy correlated closely with the E_f stabilization. PL spectra revealed a peak feature at 1.0 eV in the clean CdTe spectrum which broadened and shifted to higher energy for the Au / Yb / CdTe interface, suggesting the formation of a second emission peak near 1.1 eV. The relative intensity of this new emission increased further for the Au / CdTe interface. Previous SPS measurements indicated that the 1.1 eV transition is associated with a defect state 1.1 eV above E_v . Thus the E_f position at the Au / CdTe coincided with the deep level energy, providing direct evidence that formation of this level caused "pinning" at $E_v + 1.1$ eV. Furthermore, by limiting the formation of such discrete states via atomic-scale chemistry, one can minimize their otherwise dominant influence on the E_f stabilization and thereby control barrier heights over a much wider energy range. The significance of this result is not limited to CdTe.

We employed a second technique to suppress Te outdiffusion from CdTe, namely telluride compounds with strong ionic bonding to passivate the metal-semiconductor interface. For narrow gap semiconductors such as PbTe, an additional advantage in forming small p-type barriers is that the interlayer work function is quite large - especially if the PbTe is degenerately doped with acceptors. Preliminary results for PbTe interlayers at Au/CdTe interfaces showed an E_f stabilization even lower in the band gap than with Yb - only 0.4 eV above the valence band edge. We have confirmed this value with *in-situ* internal photoemission measurements of barrier height on the same interface as that measured by SXPS. More work is required to confirm the reproducibility of these results and to monitor their stability. Clearly, this result suggests new possibilities for controlling Schottky barriers to II-VI compound semiconductor interfaces using reacted compound layers.

We have initiated a study of the electronic properties of metals on high quality crystalline surfaces of CdTe grown by molecular beam epitaxy (MBE). From our previous work on bulk single crystals, it is apparent that crystal quality can be a major factor in the control of electronic barrier heights at metal-CdTe interfaces. Using MBE films grown under a variety of conditions by Dr. S. Sivananthan of Prof. J.P.Faurie's group at the University of Illinois, Chicago Circle, we have discovered that deep level luminescence is a sensitive indicator of MBE growth quality and potentially a powerful tool in optimizing growth conditions.

Photoluminescence spectroscopy (PLS) studies of as-grown CdTe crystal films exhibit wide variations in deep level luminescence as a function of orientation, Cd / Te flux, and growth temperature. Pronounced deep level transitions appear in spectral

regions centered around 0.8, 1.1, and 1.4 eV. The relative intensities of these features along with the band edge transition vary dramatically with growth conditions. Comparison of PLS features excited with a He-Cd (4416 Å) versus a He-Ne (6328 Å) laser reveal the presence of nonuniform distributions of deep levels with respect to the semiconductor surface. Furthermore, the densities and relative surface / bulk distributions of these deep levels are sensitive to subsequent thermal processing.

We have measured PLS and cathodoluminescence (CLS) spectra of MBE-grown CdTe specimens as a function of thermal desorption and heat treatment under ultrahigh vacuum (UHV) conditions. CdTe specimen surfaces were etched in a 0.05% Br-methanol solution to remove surface contamination, then transferred within a nitrogen-purged dry box into a UHV load lock. Chemical analysis using Auger electron spectroscopy (AES) reveals surfaces nearly free of C and O with a Te / Cd ratio in excess of 2:1. Repeated heating to 200 C reduces this ratio to stoichiometric proportions (as determined from UHV-cleaved CdTe (110) surfaces) as well as reducing the residual C and O to below detectable levels. For a CdTe (100) surface after Br-methanol etching and thermal desorption of excess Te, PLS spectra displayed a large increase in band edge luminescence and a large decrease in low energy luminescence, consistent with a clean surface with nearly flat bands and negligible interface state density. These results confirm earlier reports of clean, high quality substrate preparation (J. P. Faurie, A. Million, and G. Jacquier, *Thin Solid Films*, 90, 107 (1982)). In general, (100) surfaces exhibit much stronger near-band-edge luminescence than (111) surfaces, perhaps due to the higher growth quality of the former (J. P. Faurie and A. Million, *J. Crystal Growth* 59, 10 (1982); M. Oron, A. Raizman, H. Shtrikman, and G. Cinader, *Appl. Phys. Lett.* 52, 1059 (1988)). Similarly, near-band-edge luminescence from (111) surfaces appears to improve

with increasing growth temperature between 250 C and 335 C, also in agreement with the increase in crystal quality (G. Monfroy, S. Sivananthan, J. P. Faurie, and J. L. Reno, J. Vac. Sci. Technol. 7, 326 (1989)). The strong near-band-edge luminescence and relatively low deep level emission obtainable with MBE-grown CdTe (100) films compares favorably with that of even the best bulk bulk crystal CdTe studied to date.

We have also used PLS and CLS to characterize the production of new deep levels in MBE-grown CdTe as a function of excess thermal treatments. These spectra changed with each additional thermal treatment. For a specimen heated directly to 250 C for 60 sec following etching, an additional band appears at 0.95 eV plus only a small signal at the band edge. Heating to 350 C increases the intensity of a broad band extending below 0.7 eV and produced additional bands near 1.3 eV. The relative intensities of these new bands varied with depth, as measured via voltage - dependent CLS and wavelength - dependent PLS. Longer desorption at 350 C produced a new intense band at 1.1 eV and further increased the band edge signal. However, at this point, the surface became quite rough and spectra varied widely across the surface. Heating to 400 C produced a new band at 1.45 eV and further surface roughness. An extremely intense luminescence appeared at 0.5 eV, but only at specific locations across the surface. Heating to 450 C produced spectra with intense near band edge luminescence at 1.55 eV. Heating to 500 C destroyed (evaporated) the specimen. Correlation of these deep levels with changes in near-surface chemistry should help identify the native deep levels induced by these thermal treatments. Overall, the rich array of information obtained by PLS and CLS demonstrates the power of deep level luminescence techniques as *in-situ* probes for assessing and optimizing CdTe films grown by MBE.

In summary, the work described here demonstrates that the chemical and electronic properties of the metal / CdTe or other II-VI compound semiconductor are closely related and that atomic-scale processing techniques can be useful in controlling both the metallurgical and the Schottky barrier features of the interface. Pulsed laser processing combined with surface science techniques revealed microscopic chemical interactions at elevated temperatures for representative metal-semiconductor junctions. Optical spectroscopy techniques showed that such chemical interactions produced changes in the deep electronic levels within the semiconductor band gap. Carefully controlled measurements of both chemistry and electronics under UHV conditions established that the E_f stabilization within the semiconductor band gap was dominated by the presence of these deep levels. Essentially, these deep levels are the link between interface chemistry and Schottky barrier formation. By suppressing this chemical interaction, we were able to control the semiconductor band bending over a much wider range than hitherto possible, achieving the lowest p-type barriers to nondegenerately-doped CdTe reported to date. Finally, we have shown that these studies can be extended to CdTe films grown by MBE. For these higher quality crystals, we should be able to optimize growth and device properties with even less interference from deep levels. These results offer multiple new opportunities for further improving the chemical and electrical stability, as well as the absolute Schottky barrier heights of metal contacts to CdTe and other II-VI compound semiconductors.

**Technical Papers Published Under Army Research Office Contract
DAAL03-86-C-0003**

1. **Modification of Electronic and Chemical Structure at Au and In - CdTe Interfaces by Pulsed Laser Annealing**, J.L.Shaw, R.E.Vituro, L.J.Brillson, D.Kilday, M.K.Kelly, and G. Margaritondo, *Journal of Electronic Materials*, 17, 149 (1988).
2. **Interfacial Deep Level Formation and Its Effect on Band Bending at Metal/CdTe Interfaces**, J.L.Shaw, R.E.Vituro, and L.J.Brillson, *Journal of Vacuum Science and Technology*, *Journal of Vacuum Science and Technology* A6, 2752 (1988).
3. **Cathodoluminescence Spectroscopy of Metal-Semiconductor Interface Structures**, L.J.Brillson, R.E.Vituro, J.L.Shaw, and H.W.Richter, *Journal of Vacuum Science and Technology* A6, 1437 (1988).
4. **Deep Level Formation and Band Bending at Metal/CdTe Interfaces**, J.L.Shaw, R.E.Vituro, D.Kilday, M.Kelly, G.Margaritondo, and L.J.Brillson, *Journal of Vacuum Science and Technology* A6, 1579 (1988).
5. **Unpinned Schottky Barrier Formation at Metal/GaAs Interfaces**, L.J.Brillson, R.E.Vituro, J.L.Shaw, C.Mailhot, N.Tache, J.McKinley, G.Margaritondo, J.M.Woodall, P.D.Kirchner, G.D.Pettit, and S.L.Wright, *Journal of Vacuum Science and Technology* B6, 1263 (1988).
6. **Chemically Controlled Deep Level Formation and Band Bending at Metal-CdTe Interfaces**, J.L.Shaw, R.E.Vituro, L.J.Brillson, and D. LaGrafte, *Applied Physics Letters* 53, 1723 (1988).
7. **Influence of Deep States on GaAs and CdTe-Metal Interface Formation**, J.L.Shaw, R.E.Vituro, L.J.Brillson, and D. LaGrafte, *J. Electron. Mat.* 18, 59 (1989).
8. **Deep Levels and Band Bending at Metal-Semiconductor Interfaces**, L.J.Brillson, in *Metallization and Metal-Semiconductor Interfaces*, NATO ASI Conference Series, edited by I. Batra (Plenum, New York, 1989) in press.
9. **Interdiffusion, Interfacial State Formation, and Band Bending at Metal/CdTe Interfaces**, J.L.Shaw, R.E.Vituro, L.J.Brillson, and D. LaGrafte, *Journal of Vacuum Science and Technology*, in press.

Participating Scientific Personnel and Advanced Degrees Awarded

1. Dr. Jonathan L. Shaw

Appendices: Technical Papers